Effects of C, Cu, and Be substitutions in superconducting MgB$_2$

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Density functional calculations are used to investigate the effects of partial substitutional alloying of the B site in MgB$_2$ with C and Be alone and combined with substitution of Mg by Cu. The effect of such substitutions on the electronic structure, electron-phonon coupling, and superconductivity are discussed. We find that Be substitution for B is unfavorable for superconductivity as it leads to a softer lattice and weaker electron-phonon couplings. Replacement of Mg by Cu increases the lattice stiffness and electron count. We estimate that with full replacement of Mg by Cu and fractional substitution of B by C, $T_c$ values of 50 K may be attainable.

Here we explore some possible substitutions and give a suggestion for experimental work aimed at finding related high $T_c$ phases. Along these lines, Medvedeva et al. investigated a number of possible substitutions of Mg by monovalent, divalent and trivalent ions. They focused on the band structure, particularly the density of states (DOS) and presence or absence of the $\sigma$ band at $E_F$. They concluded that trivalent substitutions like Y, Al, etc. are not favorable as they fill the hole doped (in MgB$_2$) $\sigma$ bands, while certain monovalent substitutions for Mg may be favorable. This is consistent with the experimental observation that Al substitution destroys superconductivity. They also mentioned possible vacancies or substitutions in the B sheets, but concluded that these are all unfavorable. We briefly examine Be substitution in the sheets. Though Be lowers the electron count, superconductivity is suppressed due to a strong decrease in the lattice stiffness and a drop in the electron-phonon coupling. We then report calculations investigating the effect of a combined partial substitution of C for B and Cu for Mg. The rationale for this is that very strong C-B bonds are expected in this structure, so C substitution may lead to a stiffening of the sheets relative to MgB$_2$, while the replacement of Mg by Cu may be expected to first of all compensate for the extra charge provided by the substitution in the plane, and second, maintain the hole doping of the $\sigma$ bonding band, present in MgB$_2$ but absent in graphite. Kong et al. and Bohnen et al. reported electron-phonon calculations over the whole zone obtaining couplings consistent with the measured $T_c$ values of 50 K. They report the effect of the boron isotope effect, the specific heat enhancement, the reported gap values, and transport data. They show strong coupling between the hole “doped” bonding bands and high frequency optical phonons associated with motions of the B atoms affecting the covalent bonds.

The picture that emerges is one where the high $T_c$ is due to strong electron-phonon coupling associated with the hole doped metallic $\sigma$ bonding bands in the B sheets. The light B mass is responsible for the high average frequency of the strongly coupled phonons, setting the temperature scale. The crucial aspects for the superconductivity seem to be (1) band structure, particularly the presence of hole doped $\sigma$ bands at the Fermi level, $E_F$, (2) strong electron-phonon coupling associated with the strong covalent bonding nature of these bands, and (3) high phonon frequencies associated again with the strong covalent bonds and the light B mass.
we employ the virtual crystal approximation (VCA) to account for partial substitutions on the B sheets. A partial justification for this is provided by the strong covalency and corresponding large bandwidths, which may limit the amount of scattering due to potential disorder in the alloy (this is the same effect that allows alloys, like Al_{x}Ga_{1-x}As, to have high enough mobilities to be useful in semiconductor technology). We tested the VCA by comparing with ordered cells at the compositions MgBeB and CuBC and found some quantitative differences, but the key features of the band shapes, velocities, and the position of the σ bonding band relative to $E_{F}$ were little changed. The second approximation we made was to characterize the lattice stiffness by the calculated tensile stiffness of the B sheets, i.e., $\frac{\partial^{2}E}{\partial a^{2}}$. The variation of this number and the composition dependent mass of the sheets was used to scale the average frequencies as calculated by Kong et al.\textsuperscript{17} We use an average phonon frequency of 850 K for MgB\textsubscript{2}. Considering that the dominant phonons are the B modes, we think that this is a reasonable approximation. Finally, we use the RMTA to characterize the electron-phonon coupling.\textsuperscript{26,27}

We used DOS calculations from first principles eigenvalues at over 2000 $\mathbf{k}$ points in the irreducible zone for $N(E_{F})$ and the angular momentum components, and the self-consistent LAPW potentials at different concentrations to calculate the corresponding phase shifts and free scatterer DOS. Sphere radii of 1.5$a_{0}$ were used for B, Be, and C in the RMTA calculations. The above quantities were used in the Gaspari-Gyorffy formula to compute the Hopfield parameters, $\eta$, for each site. Negligible coupling is found on the Mg site, as expected, but not Cu, e.g., 0.78 eV/A\textsuperscript{2} on Cu for CuB\textsubscript{2}. However, in Table I we give the values of $\eta$ for B only, since that is the dominant contribution controlling superconductivity and we do not include any Cu contribution in the calculation of $\lambda$ or $T_{c}$. (Cu will have little involvement in the high frequency phonons associated with the B sheets). For the electron-phonon coupling we used the usual expression $\lambda = \eta(M\omega^{2})$. In the denominator we used the average frequency of Kong et al.\textsuperscript{17} for MgB\textsubscript{2} and scaled it using the tensile stiffness of the B sheets for various concentrations, i.e., $\frac{\partial^{2}E}{\partial a^{2}}$. The RMTA is not generally as well justified in sp metals as in transition metals and can considerably underestimate the deformation potentials when strong sp covalent bonding is present as it is here. Further, the RMTA neglects some differences between different bands, which may be significant here. In any case, Kortus et al. did use it for MgB\textsubscript{2} to characterize electron-phonon couplings.\textsuperscript{19} Our RMTA value of $\eta$ for MgB\textsubscript{2} is significantly lower than that of Kortus et al.\textsuperscript{19} We do not understand the reason for this difference, but note that their calculations were done with overlapping ASA spheres. We obtain much better agreement with a subsequent calculation by Antropov et al.\textsuperscript{21} Comparing with the direct calculations of Kong et al. for MgB\textsubscript{2} we find, not unexpectedly, that the values of $\eta$ we obtain with our nonoverlapping B spheres are too small, roughly by a factor of 3. Here we

**Table I. Properties of MgBe\textsubscript{2-x} and CuB\textsubscript{2-x}C\textsubscript{x} as obtained in the VCA.**

<table>
<thead>
<tr>
<th>$a$</th>
<th>$c$</th>
<th>$S$</th>
<th>$N(E_{F})$</th>
<th>$\eta$</th>
<th>$\lambda^{*}$</th>
<th>$T_{c}^{*}$</th>
<th>$\lambda$</th>
<th>$T_{c}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgB\textsubscript{2}</td>
<td>5.74</td>
<td>6.52</td>
<td>1.00</td>
<td>0.68</td>
<td>3.60</td>
<td>0.93</td>
<td>39</td>
<td>0.78</td>
</tr>
<tr>
<td>MgBe\textsubscript{1.5}B\textsubscript{1.5}</td>
<td>5.99</td>
<td>6.54</td>
<td>0.78</td>
<td>0.84</td>
<td>2.36</td>
<td>0.78</td>
<td>26</td>
<td>0.66</td>
</tr>
<tr>
<td>MgBeB</td>
<td>6.43</td>
<td>6.03</td>
<td>0.56</td>
<td>0.90</td>
<td>1.45</td>
<td>0.67</td>
<td>16</td>
<td>0.56</td>
</tr>
<tr>
<td>MgBe\textsubscript{1.5}B\textsubscript{0.5}</td>
<td>6.90</td>
<td>5.53</td>
<td>0.48</td>
<td>0.98</td>
<td>1.04</td>
<td>0.56</td>
<td>9</td>
<td>0.47</td>
</tr>
<tr>
<td>MgBe\textsubscript{2}</td>
<td>7.32</td>
<td>5.34</td>
<td>0.47</td>
<td>0.95</td>
<td>0.93</td>
<td>0.52</td>
<td>7</td>
<td>0.43</td>
</tr>
<tr>
<td>CuB\textsubscript{2}</td>
<td>5.58</td>
<td>6.28</td>
<td>1.11</td>
<td>1.09</td>
<td>4.38</td>
<td>1.02</td>
<td>48</td>
<td>0.86</td>
</tr>
<tr>
<td>CuB\textsubscript{1.75}C\textsubscript{0.25}</td>
<td>0.83</td>
<td>5.16</td>
<td>1.08</td>
<td>54</td>
<td>0.90</td>
<td>55</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CuB\textsubscript{1.5}C\textsubscript{0.5}</td>
<td>5.37</td>
<td>6.56</td>
<td>1.37</td>
<td>0.65</td>
<td>5.45</td>
<td>1.03</td>
<td>53</td>
<td>0.86</td>
</tr>
<tr>
<td>CuB\textsubscript{1}C\textsubscript{0.5}</td>
<td>0.50</td>
<td>3.74</td>
<td>0.68</td>
<td>24</td>
<td>0.57</td>
<td>20</td>
<td></td>
<td></td>
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<tr>
<td>CuB\textsubscript{1.25}C\textsubscript{0.75}</td>
<td>0.25</td>
<td>0.80</td>
<td>0.14</td>
<td>0</td>
<td>0.12</td>
<td>0</td>
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</tr>
<tr>
<td>CuBC</td>
<td>5.11</td>
<td>7.28</td>
<td>1.63</td>
<td>0.40</td>
<td>1.02</td>
<td>0.16</td>
<td>0</td>
<td>0.14</td>
</tr>
</tbody>
</table>

**Figure 1.** LDA band structure of MgB\textsubscript{2} with the experimental structure (solid) and calculated LDA lattice parameters (dashed). The zero is at $E_{F}$.

**Figure 2.** LDA virtual crystal band structure of MgBe\textsubscript{2-x} for $x = 1$. The lattice parameters are the calculated relaxed values. The horizontal reference at 0 denotes $E_{F}$. 

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use the RMTA to elucidate trends, while acknowledging its limitations. We adopt the heuristic of scaling the calculated values of \( \eta \) by 3 in calculating \( \lambda \) and \( T_c \). Using the average phonon frequencies quoted by Kong et al., this heuristic closely reproduces their values of \( \lambda \) and \( T_c \) for MgB\(_2\). We used the McMillan equation to roughly estimate \( T_c \), setting the Coulomb pseudopotential \( \mu^* = 0.1 \). We emphasize here that we are not aiming at an accurate determination of the value of \( T_c \) but exploring the trends upon substituting Mg by Cu and B by Be or C. If instead, we restrict the scaling of \( \eta \) to a factor of 2 and adjust the average phonon frequency to get \( T_c = 39 \) K for MgB\(_2\), we would need \( \langle \omega \rangle = 635 \) K, which is unreasonably low. Even so, the trends in \( T_c \) for the various compounds would be little changed (see Table I).

Our band structure for MgB\(_2\) (Fig. 1) is practically identical to prior results,\(^{28}\) showing \( s \) bonding states at \( E_F \). Results for the structural and electronic properties relevant to superconductivity are given in Table I, while band structures are shown in Figs. 2 and 3 for MgBe\(_{1-x}\)B\(_2\) and CuB\(_{2-x}\)C\(_x\), respectively. In the table the values of \( \eta \) are the bare values as given by the RMTA; scaled values are given for \( \lambda \) and \( T_c \) (\( \lambda^* \) and \( T_c^* \) scaling \( \eta \) by 2 instead of 3). An ordered band structure for CuBC is shown in Fig. 4. This shows some differences from the corresponding VCA calculation, most notably, near \( E_F \), a splitting at the H point involving \( p_z \) bands. However, the general structure of bands near \( E_F \) and the position of the \( \sigma \) band is quite similar.

Substitution of Be into the sheets lowers the electron count, though not in a rigid band way. The hole concentration in the \( \sigma \) bonding band does increase, but the bonds are strongly weakened. This is seen in the bandwidths and lattice stiffness. The result (Table I) is a rapid increase in \( \alpha \), softening of the lattice, and a decrease in the electron-phonon coupling. Thus Be substitution is detrimental to superconductivity.

The Cu substituted material is more interesting. In an ionic model, replacement of Mg by monovalent Cu should lower the sheet electron count by one per formula unit. However, the result differs from in-sheet Be substitution. The Cu is nominally monovalent as in the ionic model. The five narrow Cu \( d \) bands are in the valence region between \(-4\) and \(-3\) eV relative to \( E_F \). However, there is noticeable Cu \( d-B \) \( p \) hybridization, and the bands up to \( E_F \) have partial Cu character. This is reflected in the nonzero values \( \eta \) associated with the Cu site. Comparing the top panel of Figs. 1

FIG. 3. LDA virtual crystal band structures of CuB\(_{2-x}\)C\(_x\) for \( x = 0 \) (top), \( x = 0.5 \) (middle), and \( x = 1 \) (bottom). The lattice parameters are the calculated relaxed values. Note the vertical scale of the lower panel. The horizontal reference at \( 0 \) denotes \( E_F \).

FIG. 4. LDA ordered band structure for CuBC. Note the splittings relative to the virtual crystal band structure in the bottom panel of Fig. 3.
and 3 and the structural information in Table I one sees that the in-sheet bonding is strengthened by Cu substitution, even though the hole count in the $\sigma$ band is increased (note the relative positions of the band maxima on the $\Gamma$-A line). Hybridization with Cu yields quantitative band structure changes, affecting mostly the $p_z$ states, but there are also weak effects on the $\sigma$ bands near $E_F$, e.g., the reversed dispersion on the $\Gamma$-A line due to $d-p\pi$ interactions. The net effects of Cu substitution—stiffened lattice, increased $N(E_F)$ and higher hole concentration—are favorable for superconductivity. Related to this, there is a recent unconfirmed report of an enhancement of $T_c$ with partial replacement of Mg by Cu.\(^{29}\) Partial substitution of C for B in CuB$_2$ has two effects—a stiffening of the lattice reflecting the strong bonding of C and B (favorable for $T_c$) and a reduction in the hole doping of the $\sigma$ band and in $N(E_F)$ (unfavorable for $T_c$). For low C concentrations, the first effect dominates, leading to an increase in the estimated $T_c$, but beyond 25% C substitution (here the van Hove from the $\sigma$ band at $A$ crosses $E_F$) the second dominates and $T_c$ falls. Interestingly, $\lambda$ changes more slowly than $\eta$ over the high $T_c$ range. This reflects the role of bonding in the electron-phonon coupling. All things being equal, stronger bonding increases $\eta$ but also the lattice stiffness, which is the denominator of $\lambda$. Meanwhile, the prefactor of the MacMillan-Dynes formula is increased.

In summary, our calculations suggest that the $T_c$ of MgB$_2$ can be increased, perhaps to 50 K by substitution of Cu for Mg and low C substitutions, around 25%, in the B sheets. To our knowledge, CuB$_2$ in this structure does not exist. However, while we cannot show that Cu(B,C)$_2$ exists, C alloying strengthens the sheets and so the alloy may be stabilized.

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28. $N(E_F)$ in Table I is at the LDA lattice parameters for consistency and so is $\sim 4\%$ smaller than found previously with experimental lattice parameters.
29. Y. P. Sun (unpublished), as reported in Ref. 20.